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OXIDANT FORMATION IN THE GENERATION OF OZONE

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ABSTRACT

Ozone samples generated by UV photolysis and silent electric discharge upon air or oxygen were examined to determine if other oxidants were formed. Chemical and physical methods (IR and UV spectroscopy) failed to show the presence of such oxidants. Absence of such oxidants was also indicated by the excellent agreement between analytical results from UV photometry and gas phase titration. Ozone measurements by the colorimetric 1 percent neutral buffered potassium iodide method were biased 10-30 percent positive compared to UV photometry. A colorimetric method employing a solution of cyclohexene-dimethanol and ferrous ammonium sulfate (CHD), which is claimed to measure singlet oxygen and/or other oxidants along with ozone, proved to have a different stoichiometry in the presence and absence of oxygen. These latter results were interpreted to mean that the high response of CHD to ozonized air/oxygen streams does not indicate the presence of non-ozone oxidants; rather, it reflects a greater-than-stoichiometric response of the CHD reagent to ozone.

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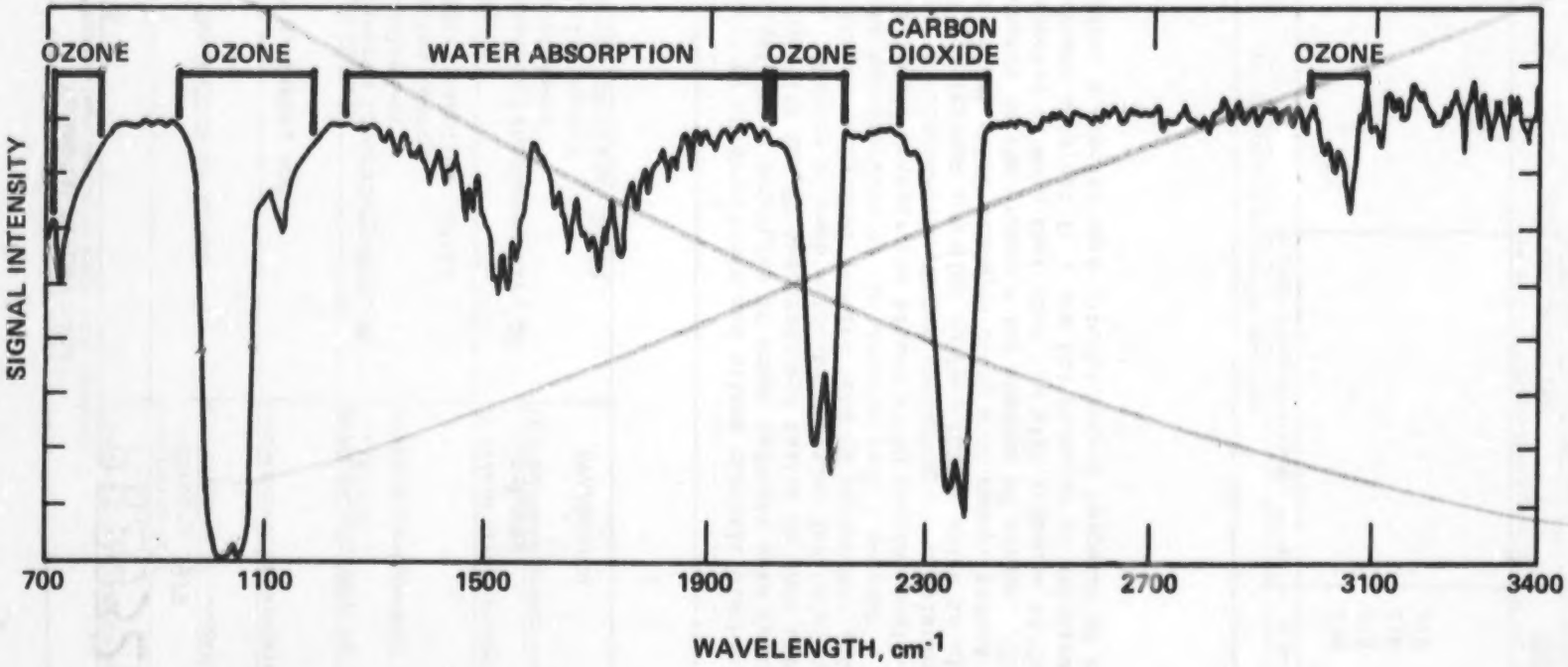
PATHLENGTH 216 meters, 760 torr



SECTION 1

INTRODUCTION

Recently, researchers at the Texas Air Control Board (TACB) used a modified ferrous ammonium sulfate-thiocyanate method containing 3-cyclohexene-1,1-dimethanol to measure ozone generated by UV photolysis or silent electric discharge of air (1). This method combined two different techniques for measuring oxidants, the olefin-singlet oxygen reaction in which a peroxide is formed (2) and the ferrous ammonium sulfate-thiocyanate technique (3). The TACB investigators found high values of oxidant when the cyclohexene-dimethanol-ferrous ammonium sulfate-thiocyanate method (CHD) was compared to the neutral buffered potassium iodide (NBKI) method for measuring ozone/oxidants generated by UV photolysis or silent electric discharge. The conclusion reached by the TACB investigators was that singlet oxygen and/or other oxidants are formed in the generation of ozone samples. Also, TACB claimed that the additional oxidant, tentatively identified as electronically excited singlet oxygen, was not measured by other standard methods such as NBKI. They speculated that singlet oxygen may be responsible for the effects observed in clinical health effects studies (4). The primary national ambient air quality standard for ozone is based on the evidence collected during these health studies. The TACB contends that the evidence may be invalid since other oxidants besides ozone were present during the health studies.

The objective of the experiments described in this report was to determine if any other oxidants are formed in the generation of ozone samples.

SECTION 2

CONCLUSIONS

The results of this study indicate:

1. The generation of ozone standards produces insignificant concentrations of singlet oxygen and no other oxidant species can be detected by a variety of measurement techniques.

2. Good agreement in ozone measurements was observed between UV photometric, gas phase titration, and NBKI methods. The NBKI method is biased in a positive direction as observed by other investigators.

3. Measurements of ozone in oxygen or air by the CHD method were always substantially (approximately 100%) higher than the NBKI method. In the absence of oxygen, ozone concentrations determined by the CHD method were lower than values determined by UV or NBKI methods.

4. The CHD method did not detect other oxidants.

5. The results of this work disagrees with the Texas Air Control Board (TACB) position that the CHD method is detecting other oxidants in air "ozonized" by UV irradiation or silent electric discharge. Rather they indicate the CHD method is not applicable to analysis of ozone and/or other oxidants in air because of a variable stoichiometry of the reagent-ozone reaction in the presence of oxygen.

SECTION 3

EXPERIMENTAL PROCEDURES

Ozone was prepared by exposing tank air or tank oxygen flowing through a quartz tube to the ultraviolet radiation from a mercury lamp (5). Ozone was also produced by flowing tank air or oxygen through a silent electrical discharge apparatus operated at 15,000 volts. The ultraviolet ozone generation system was connected to a manifold and mixing chamber system which was all glass except for a small amount of Teflon connecting tubing. Through a port upstream of the mixing chambers nitric oxide could be added. Downstream of the mixing chambers were sampling ports from which simultaneous measurements could be made. The flow of air passing through the generator and manifold system was controlled with a needle valve. Ozone produced by each of the two generation methods was also collected and sampled from 300 liter 5 mil Teflon bags.

The tank air used was low in humidity and contained less than 0.1 ppmC hydrocarbon. Two types of tank oxygen were used; one contained less than 0.2 ppmC as methane, the other contained approximately 1.4 ppmC as methane. Both oxygens were very low in relative humidity. In some experiments the air was first humidified by bubbling through distilled water in an impinger bubbler. At room temperature a relative humidity in the resulting air stream of 47% was measured on a Hygrodynamics modeled No. 15-3050 hygrometer.

Ozone in nitrogen was prepared as follows: The output from the silent electric discharge ozone generator was passed through a glass freeze out trap immersed in liquid oxygen. Ozone having a higher boiling point than oxygen condensed out as a dark blue liquid at liquid oxygen temperatures. When sufficient liquid ozone had condensed, about 0.25 ml, the ozonator and oxygen stream were turned off. Tank nitrogen was then allowed to flow through the freeze-out trap at liquid oxygen temperatures. Any oxygen in

the trap was displaced leaving ozone in nitrogen. The contents of the trap containing liquid ozone and nitrogen were transferred to an evacuated 43 liter tank by withdrawing the trap from the liquid oxygen and allowing a stream of nitrogen to carry the vaporizing ozone into the tank. The 43 liter tank and fittings were constructed of stainless steel and had been previously cleaned and conditioned with ozone in oxygen. After four trappings of ozone were tranferred, the 43 liter tank was pressurized to 60 psi with tank nitrogen. Samples of ozone in nitrogen or oxygen were prepared by metering the ozone mixture from the tank into the manifold-mixing chamber system and greatly diluting with tank nitrogen or oxygen.

Wet chemical analyses of ozone were carried out using the 1 percent neutral buffered-potassium iodide (NBKI) (6), a modified ferrous ammonium sulfate-thiocyanate method (FAST) (7), and the cyclohexene-dimethanol-ferrous ammonium sulfate-thiocyanate method (CHD) developed by the Texas Air Control Board (1). The NBKI method was standardized using a volumetrically diluted standard iodine solution. The absorbing reagent used in the CHD method was similar to that of the FAST method with the exception of added 3-cyclohexene-1, 1-dimethanol. The FAST reagent was prepared by diluting 0.25 gm of ferrous ammonium sulfate and 2.5 ml of 6N H_2SO_4 with water to 500 ml. To make the CHD reagent 2.5 gm 3-cyclohexene-1, 1-dimethanol was added to the above FAST reagent solution. To develop a color, two ml of thiocyanate reagent (5 gm ammonium thiocyanate in 100 ml water) were added to 10 ml of each of the absorbing solutions. The FAST and CHD methods were standardized with ferric ammonium sulfate standards. A plot of absorption versus ferric iron concentration for both methods gave nearly identical lines having a molar absorption coefficient of about 5800 liter/mole cm. Samples were collected in 10 ml absorbing reagent at a flow rate of 0.51 l/min. The same midget impinger bubblers were used for each individual method throughout the experiments. Colorimetric measurements of resulting solutions were made using matched one cm cells in a Cary 14 spectrophotometer. The absorption of the NBKI solutions were read immediately after sampling at a wavelength of 3520 Å. The FAST and CHD solutions were read 10 minutes after sampling at a wavelength of 4800 Å.

Ozone concentrations were determined with a modified (8) Dasibi model 1003-AH instrument which measures the absorption of ozone in the ultraviolet spectra region. The ultraviolet absorption of ozone samples were also examined in a laboratory built UV system. The system consisted of a deuterium lamp, a long path multi-pass optical glass cell, associated input and output optics, scanning monochrometer, and detector. This system was used to scan the ultraviolet region of the spectrum looking for unusual absorptions due to oxidants other than ozone. Ozone generated in air or oxygen was also examined by long path Fourier transform infrared spectroscopy to determine oxidants other than ozone which might be present. This IR equipment has been described elsewhere (9).

Ozone generated in dry or humidified air or oxygen was examined for peroxides by bubbling through distilled water to absorb any peroxides. The resulting solution was analyzed with a newly developed method for hydrogen peroxide. This method measures the chemiluminescence produced in the reaction between luminol, a catalyst and peroxide in a basic solution (10). Using an impinger bubbler with 10 ml water, samples were collected at a flow rate of 0.5 l/min.

In the gas phase titration of ozone a Bendix NO_x chemiluminescent analyzer was used to measure the nitrogen dioxide produced in the reaction of ozone with nitric oxide. In the titration experiments nitric oxide from a cylinder containing 49.3 ppm NO in nitrogen was metered into the ozone air stream.

Formaldehyde samples used to test interference in the CHD method were prepared by heating alpha-polyoxymethylene and diluting with tank air. The chromotropic acid method was used to determine the concentration of the formaldehyde sample (11).

Nitric oxide and NO_2 samples were prepared using tank air and laboratory grade chemicals. Nitric acid vapor was prepared by vaporizing ACS certified concentrated nitric acid and diluting with tank air.

SECTION 4

RESULTS

Simultaneous measurements of ozone generated at various concentrations in an air stream are shown in Figure 1. A typical comparison of ozone concentrations measured by gas phase titration and UV photometry is shown in Figure 2. The slope of the curve is approximately unity indicating an excellent agreement between the two methods. Ozone concentrations measured by the CHD method were nearly 100 percent higher than measurements made by NBKI, UV photometric or gas phase titration methods. In these experiments ozone values obtained with the NBKI method were higher by approximately 10 percent when compared to UV photometry.

Ozone was also generated in the two types of tank oxygen available, one contained less than 0.2 ppm and the other contained approximately 1.4 ppm carbon as methane. When tank oxygen was substituted for tank air, the ozone generator was adjusted to produce the same ozone concentration as was produced in tank air as measured by UV photometry. The resulting values of ozone concentration in the oxygen system as measured by the CHD and NBKI methods were essentially unchanged from results using tank air, i.e., NBKI values were 10 percent higher and CHD values 100 percent higher.

In other experiments tank air and tank oxygen were humidified to 47 percent by bubbling through distilled water in a glass impinger bubbler. Ozone, generated by the UV photolysis of the humidified air or oxygen was determined by UV photometry, NBKI, and CHD methods. The results were essentially the same as those shown in Figure 1.

Ozone prepared in nitrogen was slowly metered out of the stainless steel tank into a glass manifold system and greatly diluted with tank nitrogen (N_2) or tank oxygen. The results of three samples so prepared in nitrogen are listed in Table 1.

TABLE 1. OZONE MEASUREMENTS IN NITROGEN, $[O_3]_{ppm}$

METHODS		
UV Photometry	NBKI	CHD
0.600 ppm	0.719 ppm	0.381 ppm
0.800 ppm	1.005 ppm	0.383 ppm
1.730 ppm	2.211 ppm	0.493 ppm

Ozone in nitrogen at a concentration of 0.816 ppm as determined by UV photometry resulted in a concentration of 0.357 ppm by CHD and 0.09 ppm by FAST methods. In another experiment tank nitrogen was replaced with tank oxygen as a diluent gas in the system. UV photometric measurements indicated 0.811 ppm ozone in this sample while NBKI measurements indicated 1.011 ppm and CHD 1.708 ppm.

Ozone in oxygen was stored in a 300 liter Teflon bag and sampled over a period of 4 hours. These experiments were performed in order to establish; (1) the stability of ozone in Teflon bags and (2) note if other oxidants i.e. other than ozone, would be detected because of different stabilities of these oxidants upon standing. The ozone in this experiment was generated by silent electrical discharge in tank oxygen containing approximately 1.4 ppm carbon as methane. The results of this experiment are shown in Table 2.

TABLE 2. MEASURED $[O_3]_{ppm}$ FROM TEFLON BAG

Time	METHOD			
	UV	NBKI	CHD	CHD/UV
0	1.155 ppm	1.267 ppm	2.161 ppm	1.871
45 min	1.014 ppm	1.193 ppm	2.064 ppm	2.035
260 min	0.360 ppm	0.410 ppm	0.736 ppm	2.044

A high concentration of ozone was generated by slowly flowing dry tank oxygen through a silent electrical discharge apparatus. A concentration of 43 ppm ozone was achieved by diluting to one atmosphere the output of the ozone generator with tank oxygen into an evacuated 690 liter infrared absorption cell. Shown in Figure 3 is the infrared spectrum of this sample between the spectral region of 700-3400 cm^{-1} at a path length of 216 meters. The main absorption band at 1050 cm^{-1} is off scale at this path length with such a high concentration. The first overtone of the 1050 cm^{-1} absorption band is seen in the 2100 cm^{-1} region. Absorption bands of lesser intensity are observed at 720, 1120, and 3050 cm^{-1} regions. Absorption bands due to atmospheric water (1250-2010) and carbon dioxide (2250-2400) are also observed. These were caused by absorption in the optical path exterior to the absorption cell.

The ultraviolet absorption spectrum of ozone generated by silent electrical discharge in oxygen was observed over the 2000 to 3600 Å spectral region in a 18.3 meter multipass absorption cell. The spectrum did not exhibit any unusual absorption associated with species other than ozone.

Humidified oxygen used as a blank and ozone generated in humidified oxygen were bubbled through distilled water to absorb peroxides. The resulting aqueous solutions were analyzed for peroxides by measuring the chemiluminescence developed in the reaction with luminol. The blank solution resulted in a chemiluminescence response equivalent to 2.8 ppb H_2O_2 and the ozone sample equivalent to 4 ppb H_2O_2.

Using the CHD method, no increases in absorbance above that of the blank were observed after 5 liters of each of the following compounds in air were bubbled through the CHD absorbing solution: 0.36 ppm CH_2O, 1 ppm NO, 0.54 ppm NO_2, about 1 ppm HNO_3.

SECTION 5

DISCUSSION

SINGLET OXYGEN - $O_2(^1\Delta g)$

It was claimed by the TACB that singlet oxygen O_2 ($^1\Delta$ g) is also formed in the generation of ozone at concentrations equal to or greater than that of ozone. Two electronically excited singlet molecular oxygen species, O_2 ($^1\Delta$ g) and O_2 ($^1\Sigma$ g^+), can be produced by the absorption of light by O_2.

$$O_2 + h\nu \rightarrow O_2\ (^1\Delta\ g) \sim 12{,}700\ \text{Å} \qquad (1)$$

$$O_2 + h\nu \rightarrow O_2\ (^1\Sigma\ g^+) \sim 7600\ \text{Å} \qquad (2)$$

Singlet oxygen can also be produced by electronic energy transfer from electronically excited NO_2 molecules formed by absorption of light of wavelengths greater than 4000 Å,

$$NO_2^* + O_2 \rightarrow NO_2 + O_2\ (^1\Delta\ g) \qquad (3)$$

and by ozone photolysis in the wavelength range 2000-3200 Å (12). Ozone generated by UV photolysis from the 184.9 nm line of a mercury lamp will also be dissociated to singlet oxygen by the photolysis of ozone at 253.7 nm. Based upon steady state approximations the concentration of singlet oxygen formed in a photochemical ozone generator is estimated to be about 7% of ozone (13). The principal decay mode of singlet oxygen is by collisional deactivation with ground state oxygen.

$$O_2\ (^1\Delta\ g) + O_2\ (^3\Sigma\ g) \rightleftharpoons 2O_2\ (^3\Sigma\ g) \qquad (4)$$

The rate of this reaction is very fast with a rate constant of $k = 2.2 \times 10^{-18}$ cm^3 $mole^{-1}s^{-1}$ (14).

In calibration experiments the output of an ozone generator is transported through glass tubing to a manifold-mixing chamber system and through glass or Teflon lines to the absorbing reagent. Typical residence times between the generator and absorbing reagent are 5-15 seconds. Once the ozonized air leaves the generator at slightly above atmospheric pressure, the singlet oxygen decay can be described mathematically in the following way since molecular oxygen in reaction (4) above is in large excess when compared to the singlet oxygen concentration.

$$\frac{C}{C_1} = e^{-k[O_2]t}$$

where C = singlet oxygen concentration at any time t

C_i = initial singlet oxygen concentration

Using an $[O_2] = 5 \times 10^{18}$ molecules per cubic centimeter for a 20% oxygen system and the rate constant of the reaction, the above expression becomes:

$$\frac{C}{C_i} = e^{-11\ t}$$

With a steady state singlet oxygen concentration in the ozone generator of 7 percent of the ozone concentration one can calculate the ratio of singlet oxygen to ozone at any point in time downstream using the above expression. After one second the singlet oxygen to ozone ratio would be 1.1×10^{-6}; after 5 seconds the ratio would be 1.3×10^{-24}. Thus the concentration of singlet oxygen reaching the absorbing reagent would be insignificant.

HYDROGEN PEROXIDE - H_2O_2

Experiments were carried out under conditions which would be most favorable for peroxide formation, such as, humidifying the air or oxygen stream prior to generating ozone. High concentrations of ozone were generated and its infrared spectrum was studied. The resulting infrared spectrum was not significantly different from that shown in Figure 3 where only a small amount of water vapor was present. If hydrogen peroxide or other peroxides were formed at substantial concentrations (concentrations 1/10 less than ozone) the infrared spectrum would exhibit prominent absorption in the

1250 cm^{-1} region of the spectrum. These absorptions are definitely absent. The infrared spectrum is relatively clean and all absorption bands present are accounted for.

Tests for hydrogen peroxide and other peroxides were conducted by bubbling the ozone sample through water to trap the peroxide. The resulting solutions were analyzed using a chemiluminescent method which can detect sub ppb quantities of peroxide. A maximum value of less than 2 ppb peroxide equivalents were observed for solutions through which 15 liters of sample were bubbled. This concentration is an insignificant amount and might be due to instrument variability.

OTHER OXIDANTS - Ozonides - Unstable Species

Other oxidizing species could be ozonides (15-17) formed in the reaction of ozone with olefinic compounds in the gas stream. Unlike the experiments conducted by the TACB in which employed filtered room air, the experiments carried out in this study used tank air or oxygen essentially free of hydrocarbons, except for one tank of oxygen which contained methane. Air free of hydrocarbons is a necessity in the generation of ozone standards (5). The formation of ozonides was not observed in the infrared spectrum even when oxygen containing 1.4 ppmC as methane was used. It should also be pointed out that both H_2O_2 and organic peroxides do react with NBKI solution (18). However, as stated above, no H_2O_2 was observed in our studies and, the organic peroxides could not exist as very high concentrations since the organic carbon concentration was very low.

Using a Teflon bag as a static reactor, ozone samples were allowed to stand and decay. These experiments would detect the presence of reactive species if their lifetimes are either longer or shorter than that of ozone. Data shown in Table 2 indicate that the ratio of CHD to UV values remained nearly constant at about 2 over 260 minutes. The constant ratio indicates that either the reactive species have the same lifetime as ozone or that no other reactive species are present. The latter is the more reasonable conclusion since all other experiments had shown that no other oxidants are present and it is doubtful that two compounds have exactly the same lifetime under these experimental conditions.

Long path ultraviolet spectroscopy failed to show any unknown absorbances due to species other than ozone in the generation of ozone standards. Although the values and calculations are not reported in this text, ozone concentrations measured by long path infrared and long path ultraviolet spectroscopy were in excellent agreement.

CYCLOHEXENE-DIMETHANOL (CHD) METHOD

The CHD method used by TACB is essentially the FAST method in which 3-cyclohexene-1,1-dimethanol has been added. The olefinic compound 3-cyclohexene-1,1-dimethanol had been added to presumably react with singlet oxygen or other oxidants to form peroxides that oxidize the ferrous ammonium sulfate reagent. The reaction of singlet oxygen with an olefinic compound has been shown to produce a peroxide. Peroxides are particularly responsive to the ferrous ammonium sulfate absorbing reagent. However, singlet oxygen exists only at very low concentrations and cannot be responsible for the increased response of the CHD reagent.

Because all experimental results failed to indicate the presence of oxidants other than ozone, additional experiments were carried out to determine why the CHD method had an increased sensitivity to ozone. As a method of examining the stoichiometry of the CHD method, ozone samples were prepared in nitrogen. The results from Table 1 show that in the absence of oxygen, ozone concentrations determined by the CHD method were substantially lower. The UV photometric, NBKI, and FAST methods were unaffected by the absence of oxygen. These differences in CHD results when ozone is measured in nitrogen as compared to oxygen clearly point to a serious problem of the variability of stiochiometry. Others have observed a difference in the stoichiometry of olefin-ozone reactions in the presence and absence of oxygen (19). Although we do not know the exact number of sequence of reactions operative in the CHD method, the presence of oxygen apparently affects the ozone-cyclohexene-dimethanol reaction stoichiometry. Thus, the presence of molecular oxygen gives rise to more than one peroxide for every ozone molecule consumed. This increase in peroxide formation would be responsible for the increased oxidation of the ferrous ammonium sulfate reagent which given rise to the higher values obtained using the CHD method.

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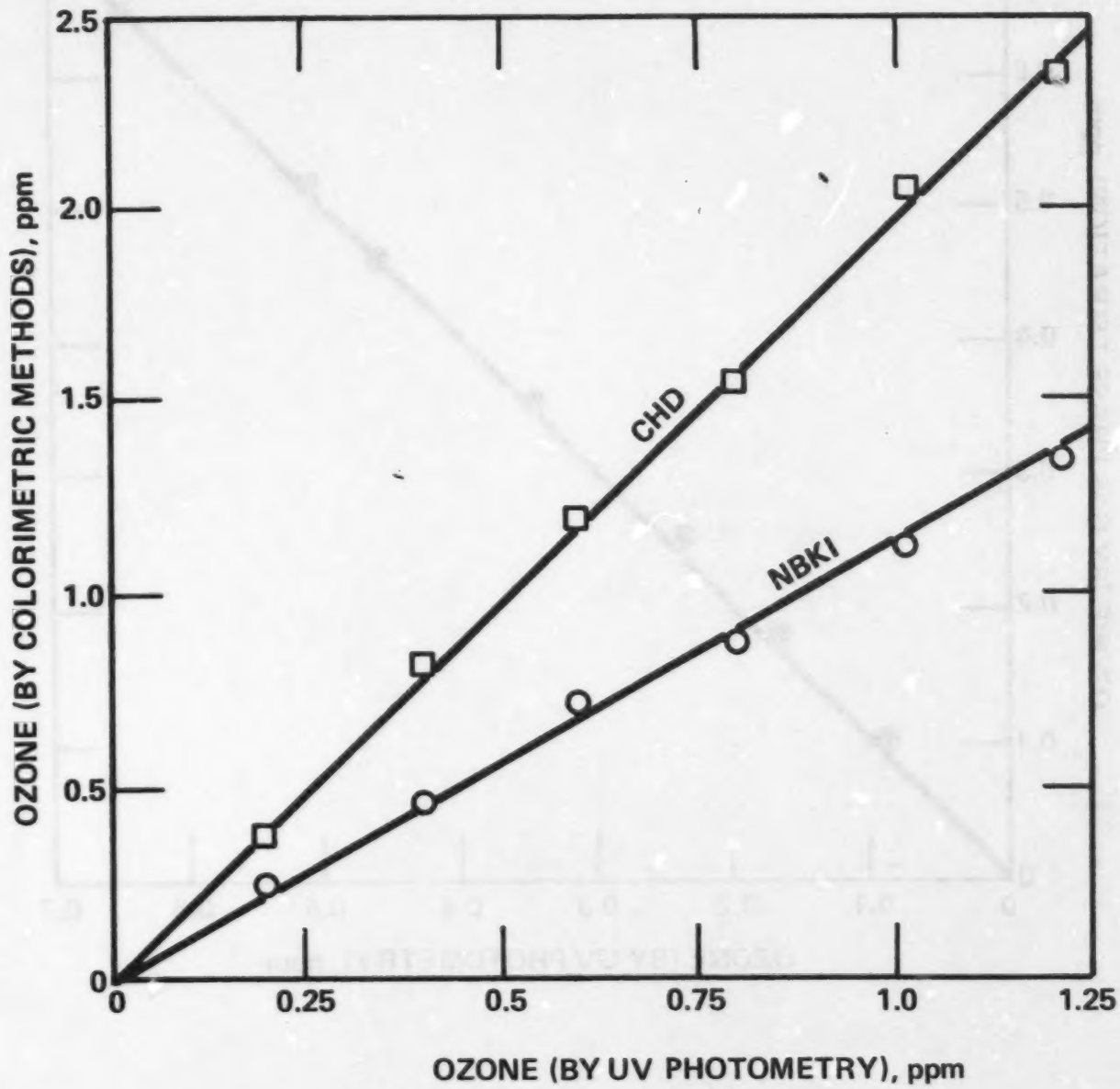
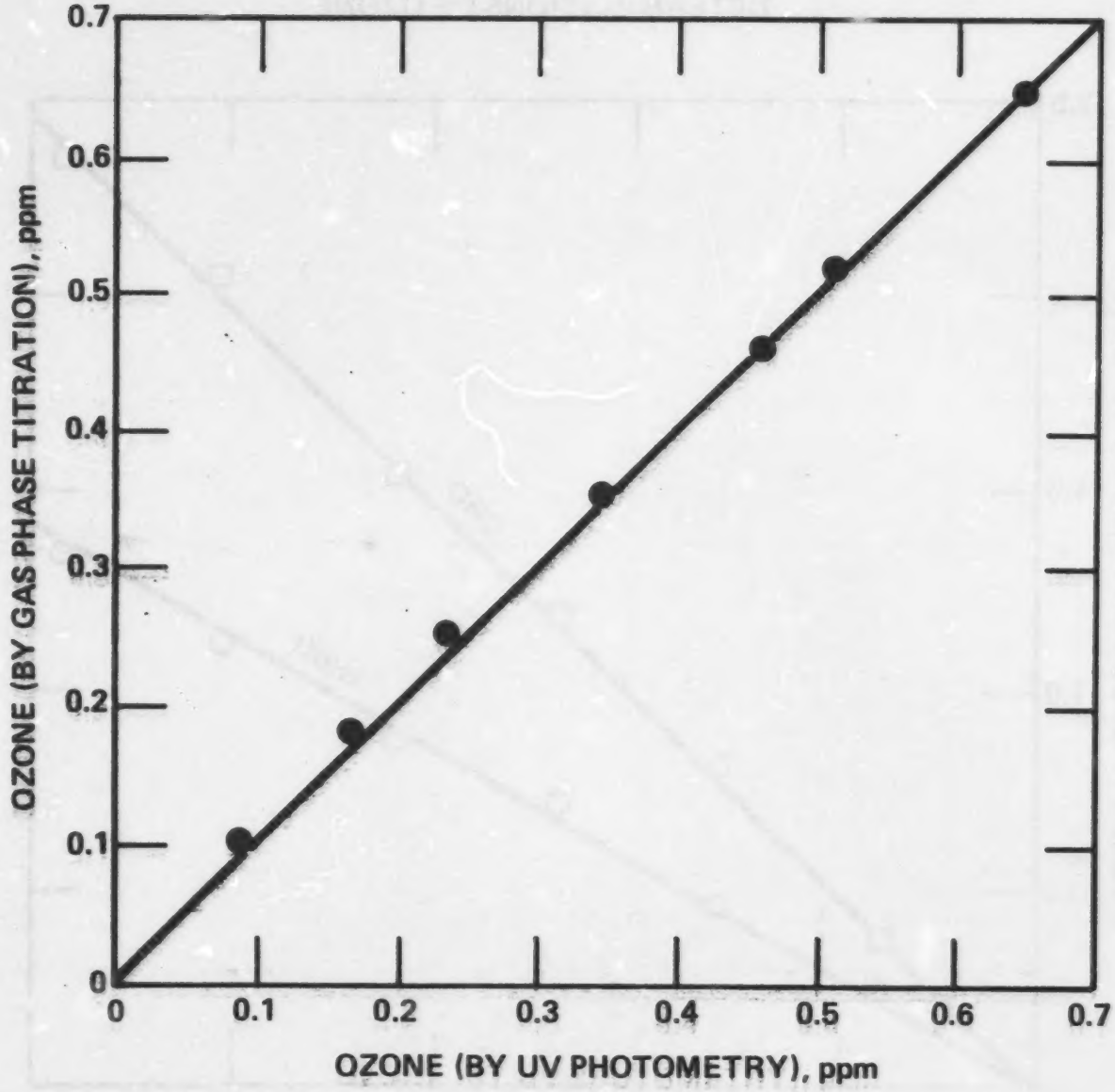
COMPARISON OF COLORIMETRIC AND UV PHOTOMETRIC DETERMINATIONS OF OZONE



COMPARISON OF GAS PHASE TITRATION AND UV PHOTOMETRIC OZONE DETERMINATIONS



SPECTRUM OF OZONE (43 ppm) PRODUCED BY SILENT ELECTRICAL DISCHARGE IN OXYGEN,
PATHLENGTH 216 meters, 760 torr